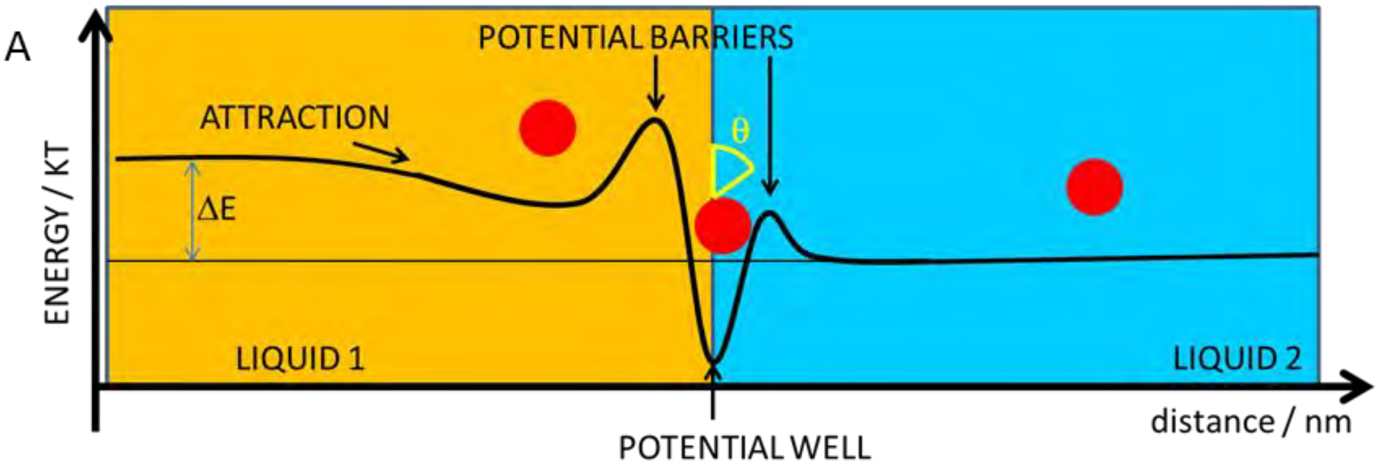
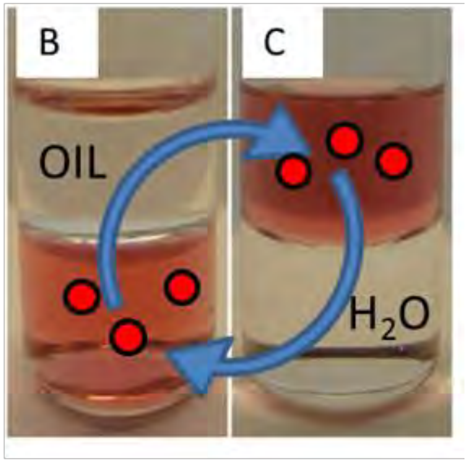
Nanoparticle Adsorption and Crossing of Fluid interfaces





A. Stocco[1], D. Wang[2]

1. ICS CNRS, Strasbourg, France

2. Jilin University, China

(2010…2015)

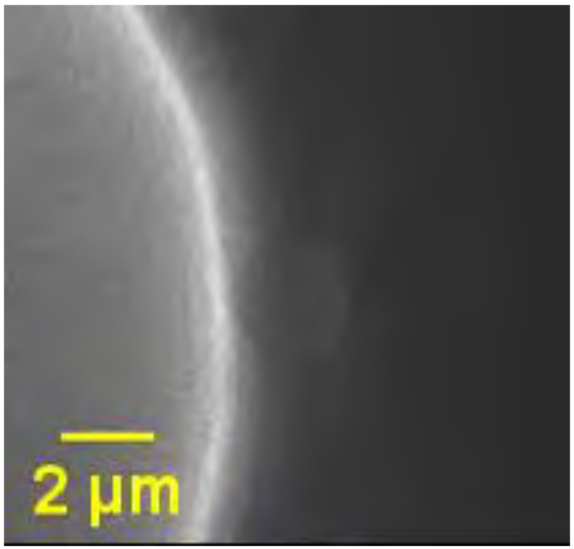
Postdoc (MPI-CI, Germany)

"***Phase transfer of nanoparticles across liquid-liquid interfaces***",
D. Wang, H. Möhwald

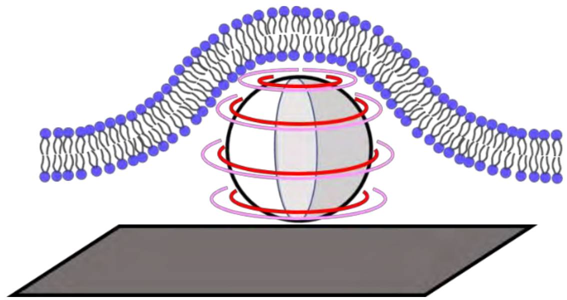
Context: Particle interacting with Interface/Membranes

Entry of Microparticles into Giant Lipid Vesicles by Optical Tweezers

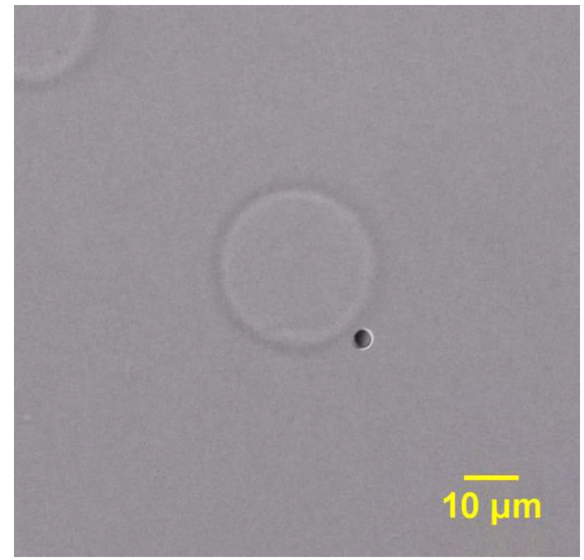
Dynamics of Active Colloid Engulfment by Giant Lipid Vesicles



Silica R_P = 1 µm
POPC Giant Vesicle



Rotational and Translational Drags of a Janus Particle Close to a Wall and a Lipid Membrane



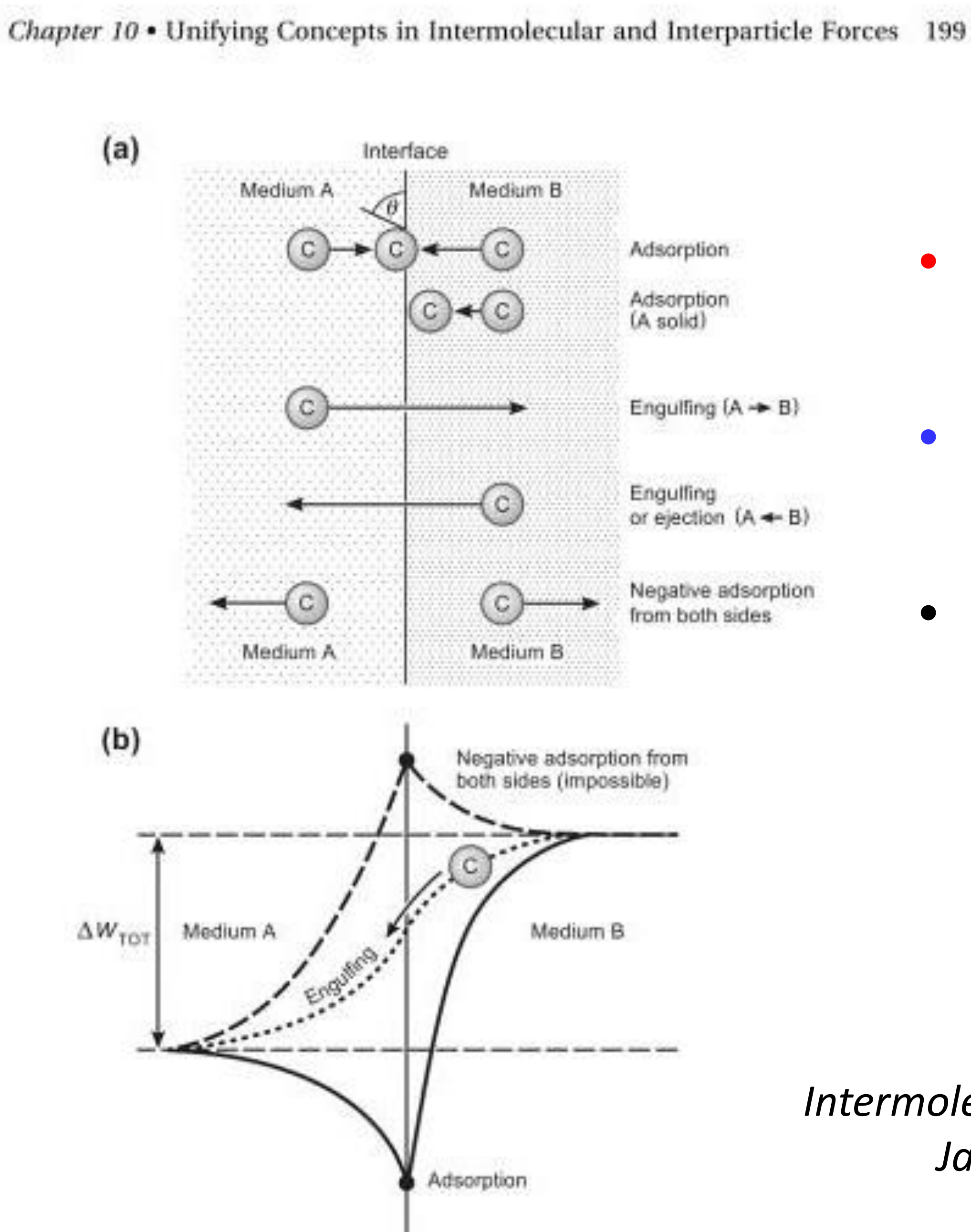
Cu/Silica R_P = 1 µm
POPC Giant Vesicle

Fessler et al.
Phys. Rev. E 107, L052601 (2023)

Sharma et al.
Journal of Colloid and Interface Science, Volume 652, 2159-2166 (2023)

Fessler et al.
In preparation

Energy Landscape across an Interface



- Adsorption
- Engulfing - Crossing
- Negative Adsorption

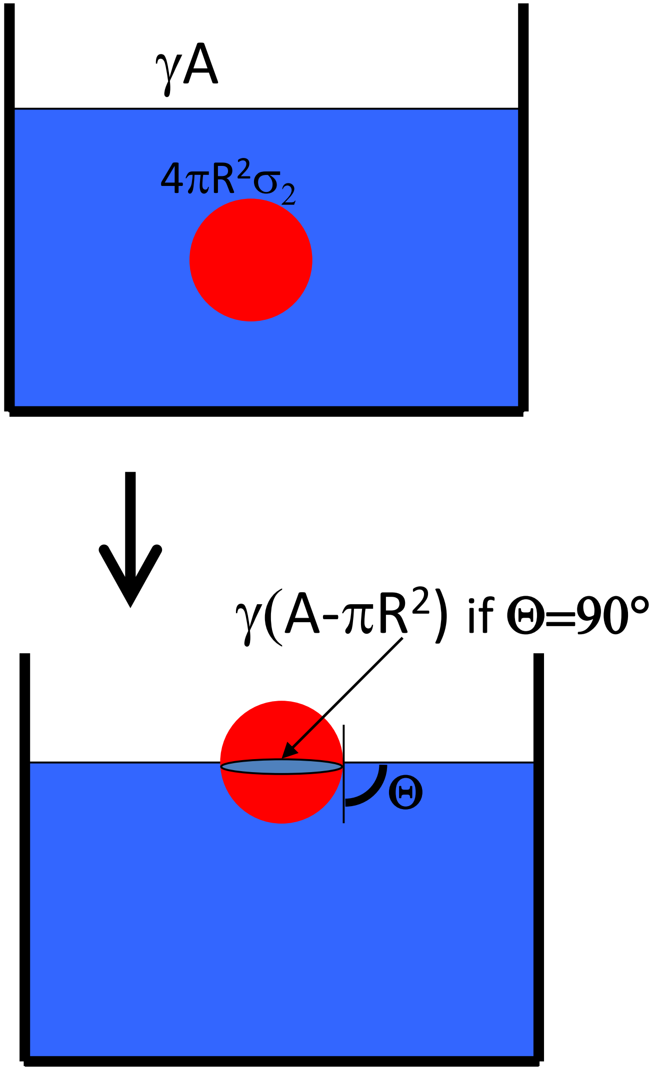
Intermolecular and Surface Forces:
Jacob N. Israelachvili

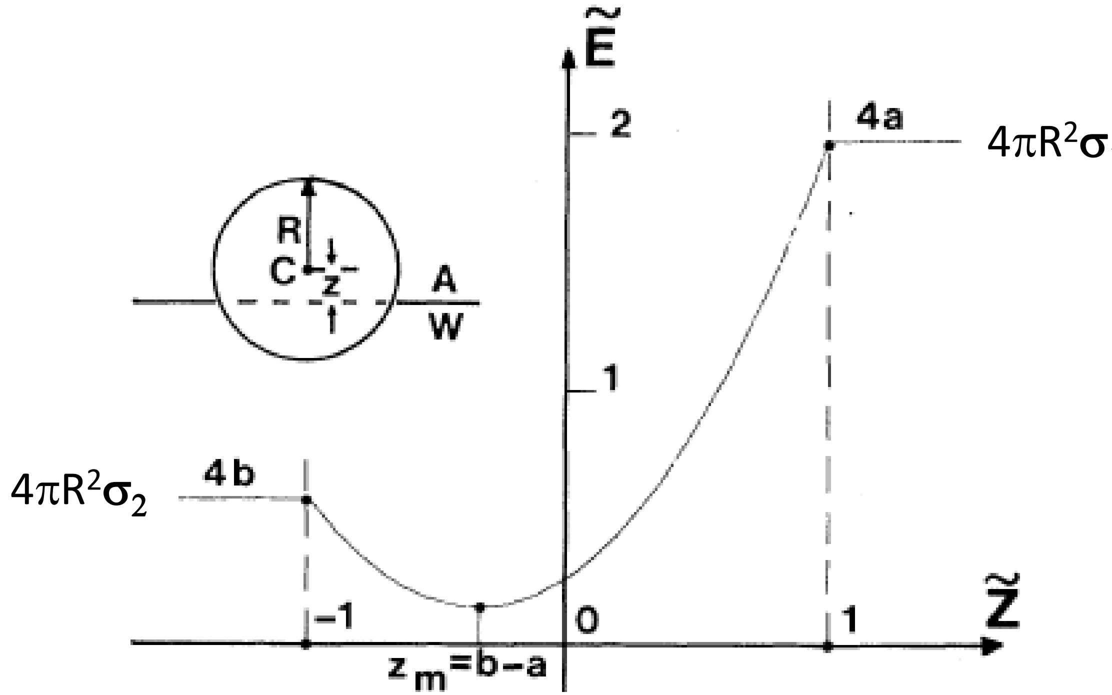
Wetting *vs* Colloidal Forces: Large Length Scale

- Macroscopic view:

Wetting energy (Interface + Particle)

P Pieranski PRL 1980,
BP Binks…





Θ = particle contact angle

min(E), $z_m/R = \cos\Theta = (\sigma_2-\sigma_1) / \gamma$

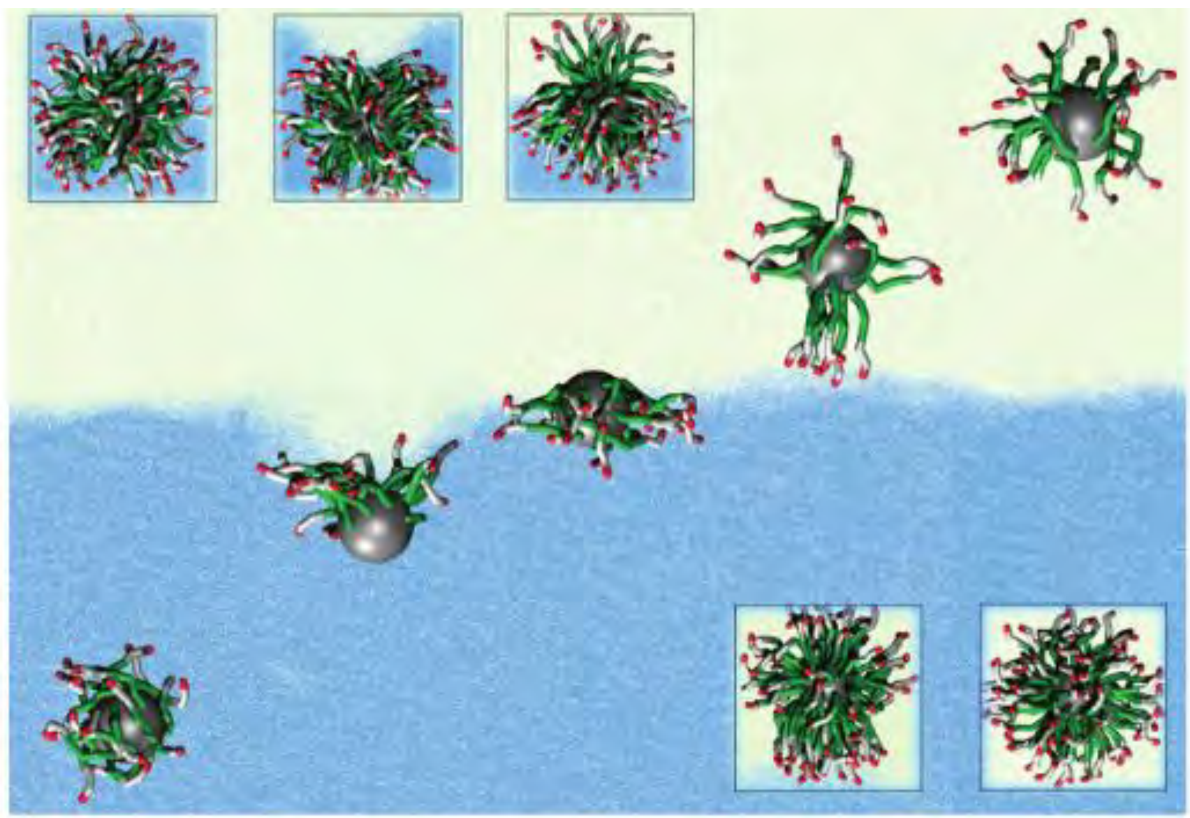
$-\Delta E_w = \pi R^2 \gamma (1 \pm \cos\Theta)^2$ =ca. 1000 kT (if R = 10 nm)

Wetting *vs* Colloidal Forces: Small Length Scale

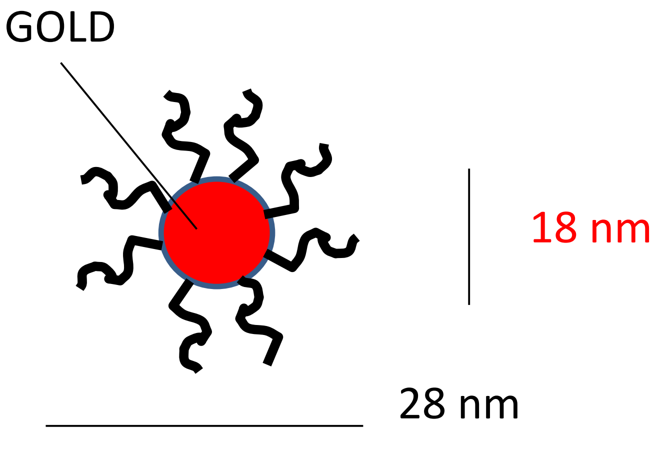
- Nanoscopic view: Van der Waals and Electrostatic, Hydrophobic and Solvent-surface groups Interactions

J. Phys. Chem. C, Vol. 114, No. 28, 2010

$-\gamma\pi R^2$?

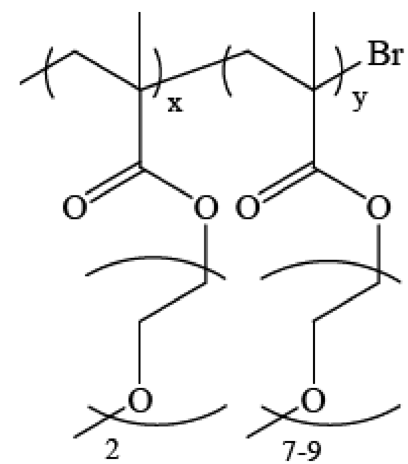


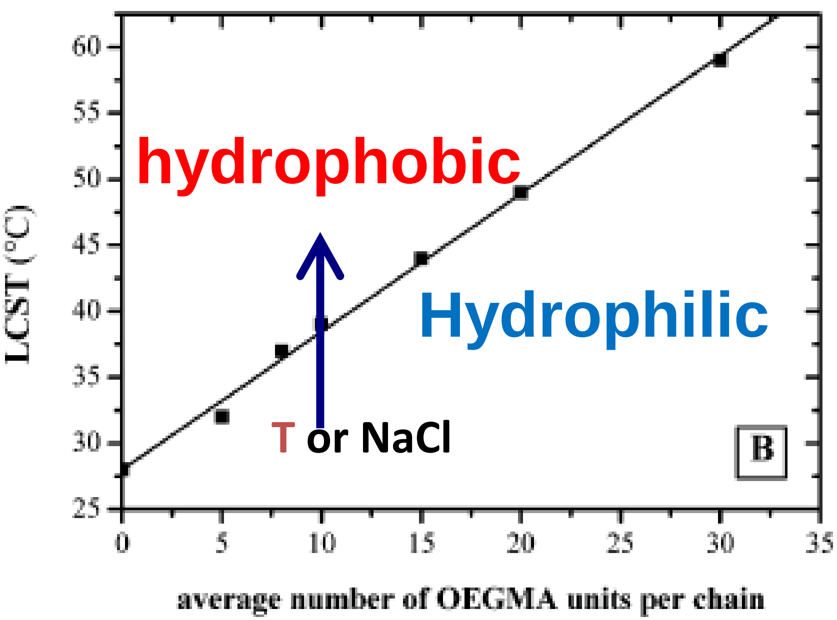
Experiment: Polymer coated Nanoparticles



PMMA- PEG- based Copolymer Shell

Poly(MEO_2MA_x-co-$OEGMA_y$)
x= 90, y = 10





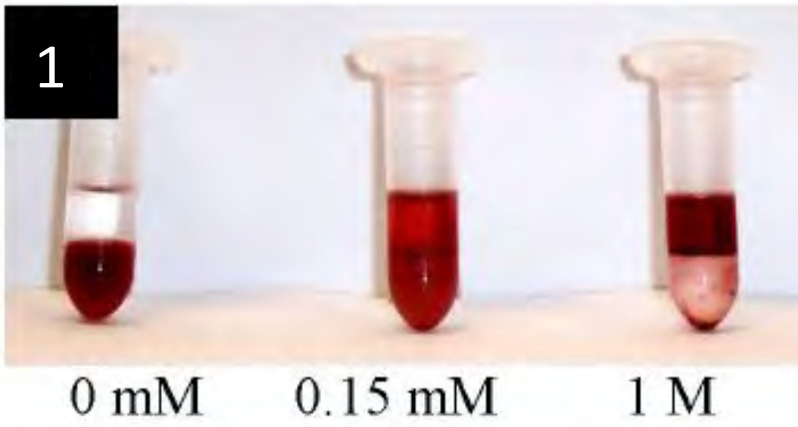
Responsive to **T** and ionic strength (**NaCl**)

JF Lutz. J. Polymer Sci. A '08

Edwards et al. Angewandte Chemie 2008

Crossing Observations

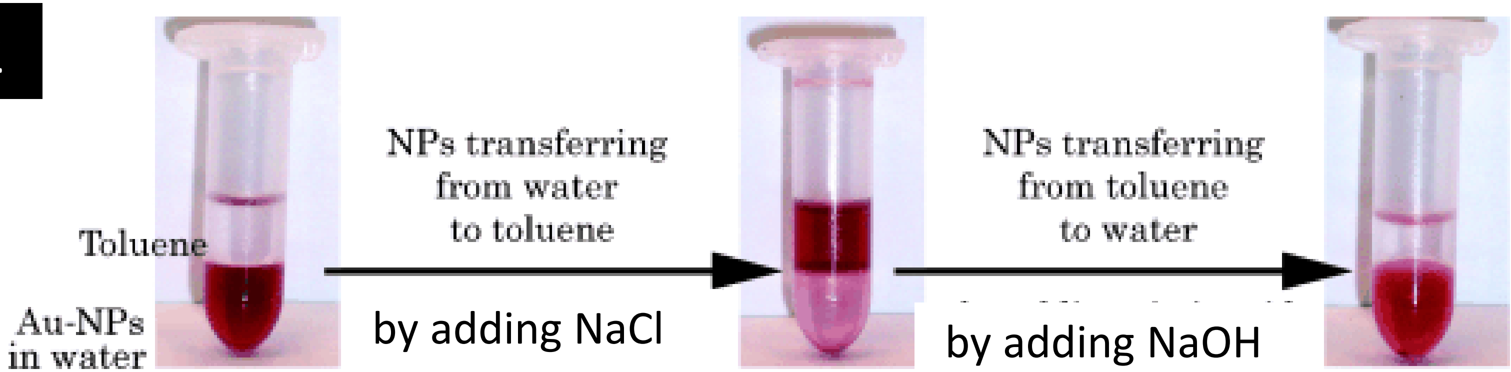
1



Water to Toluene
at room T by adding NaCl salt

Replacing salty water with pure water,
NO reversible transfer!

2



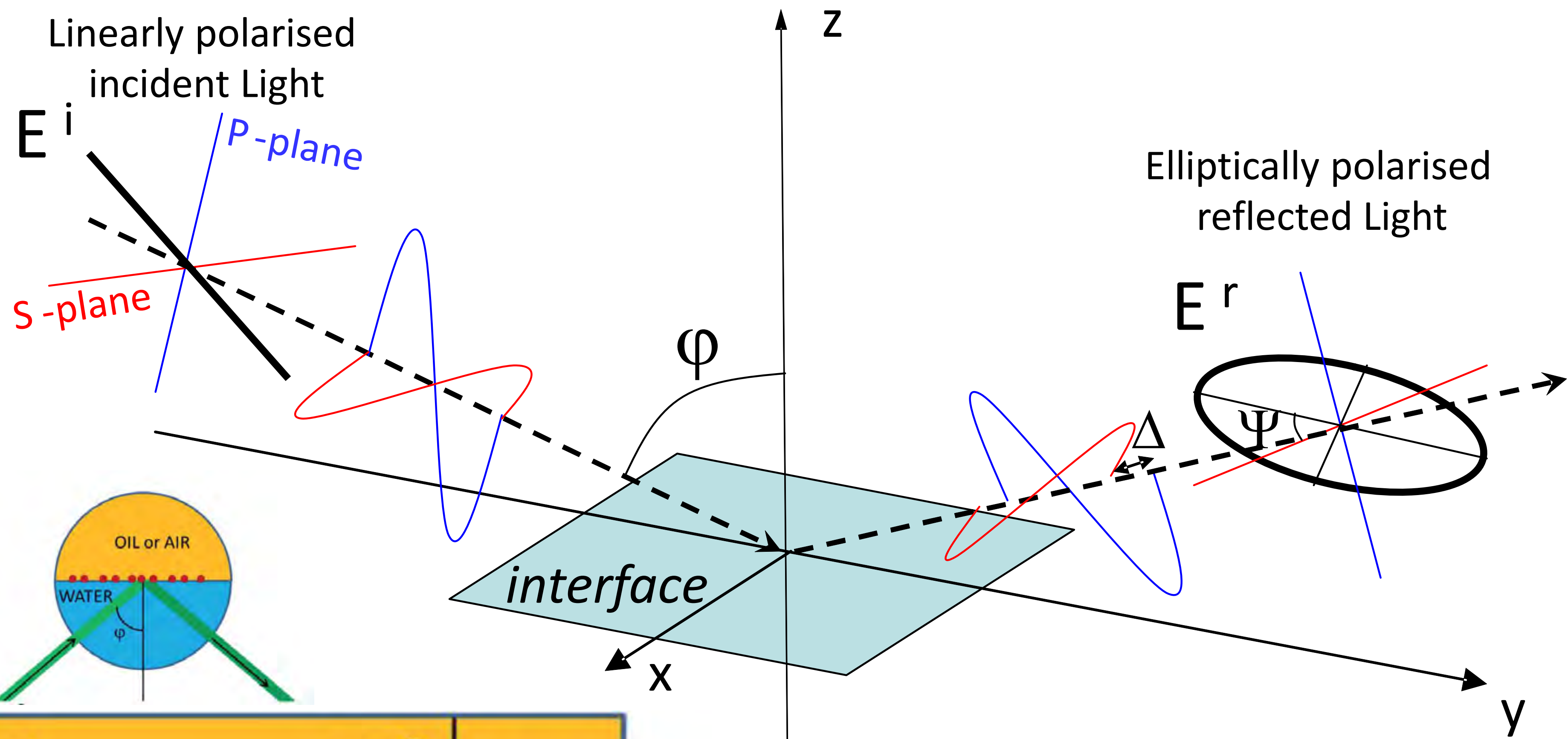
by adding NaCl

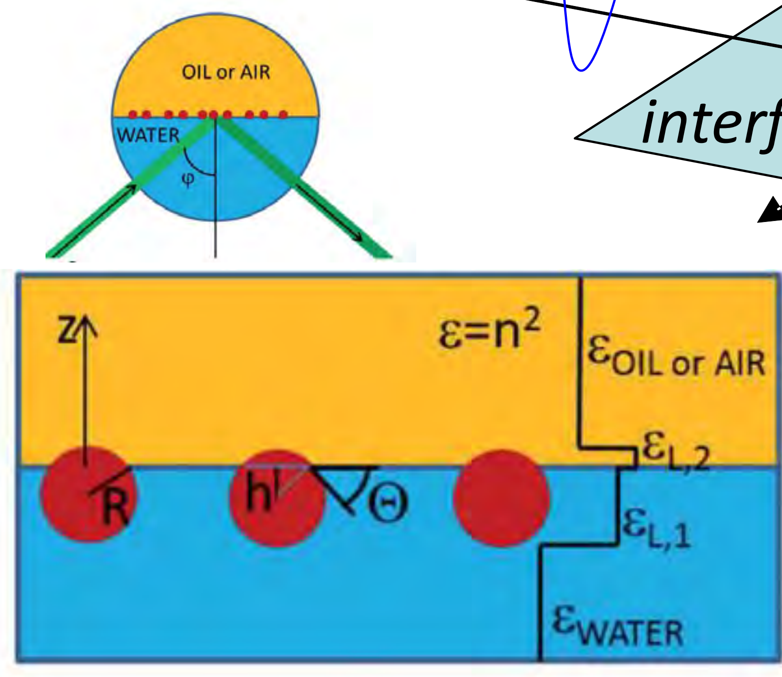
by adding NaOH
(or by low T = 5°C)

NP Free energy E (+NaOH) < E(in Toluene) < E (in Water)

Edwards et al. Angewandte Chemie 2008

Ellipsometry: non invasive, in-situ Adsorption



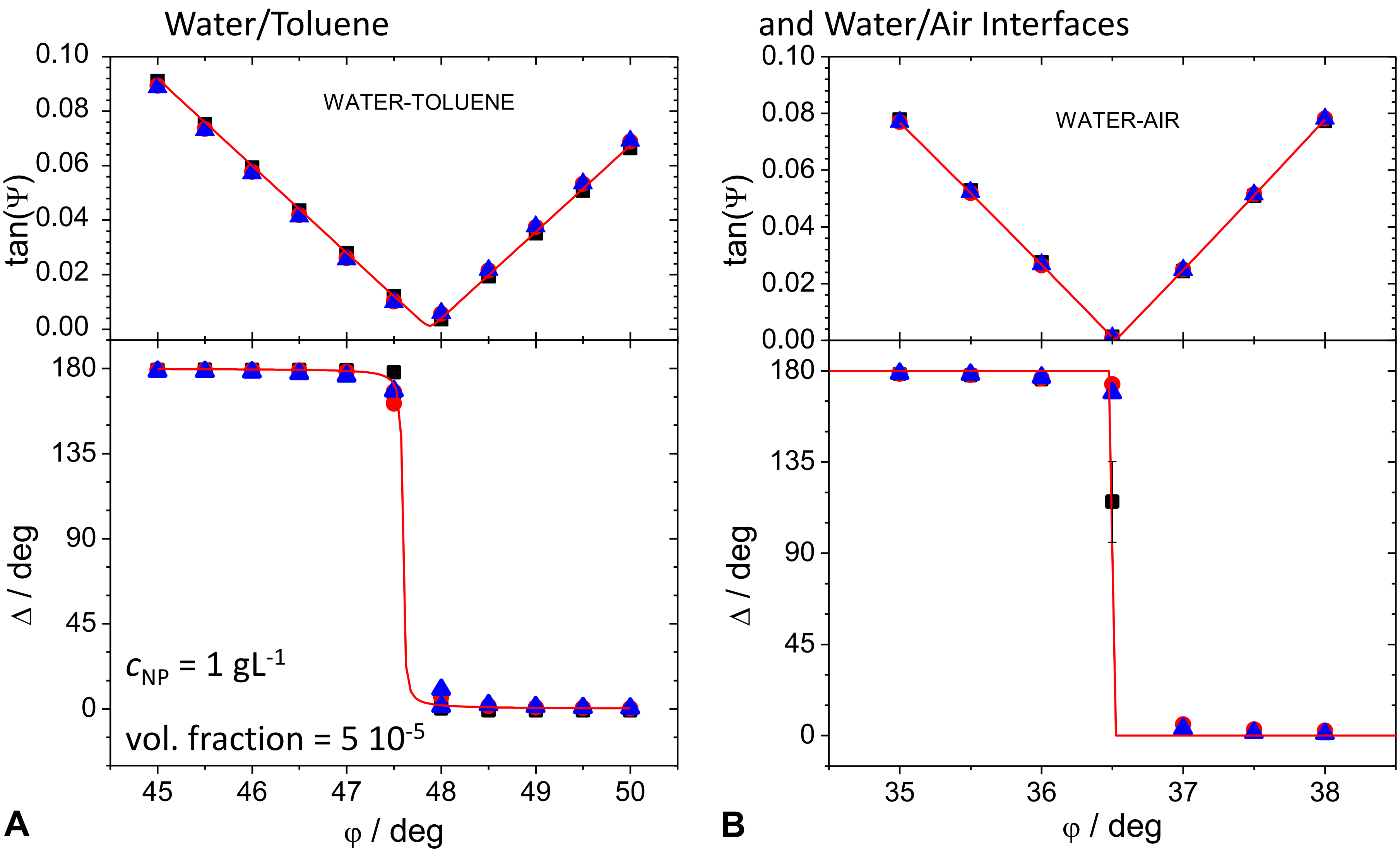


Interfacial profile model

Contact angle Θ and surface coverage ϕ

Stocco et al. Soft Matter 2014

NO Spontaneous adsorption in pure Liquids

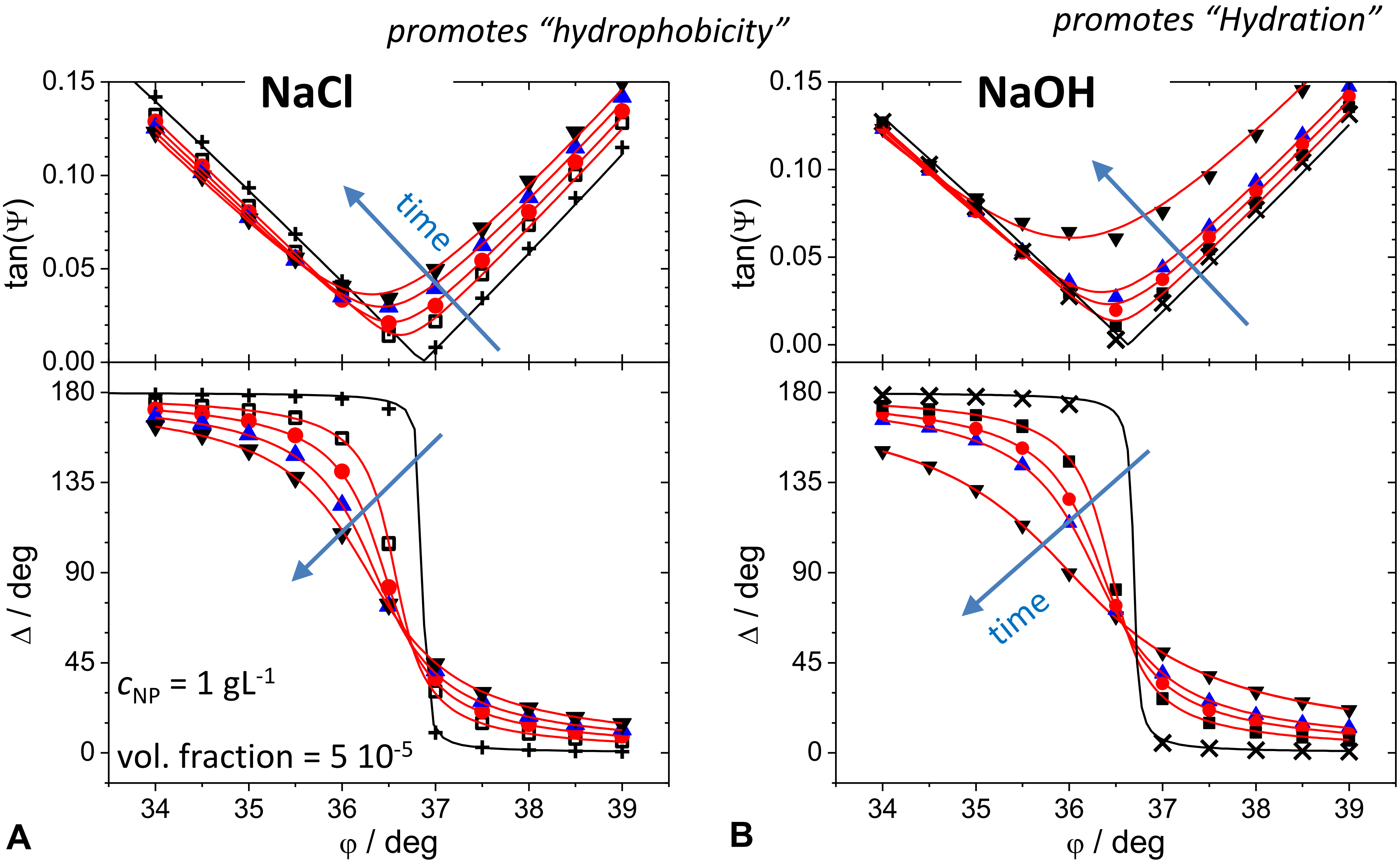


NO significant changes, NO ADSORPTION !

Stocco et al. Soft Matter 2014

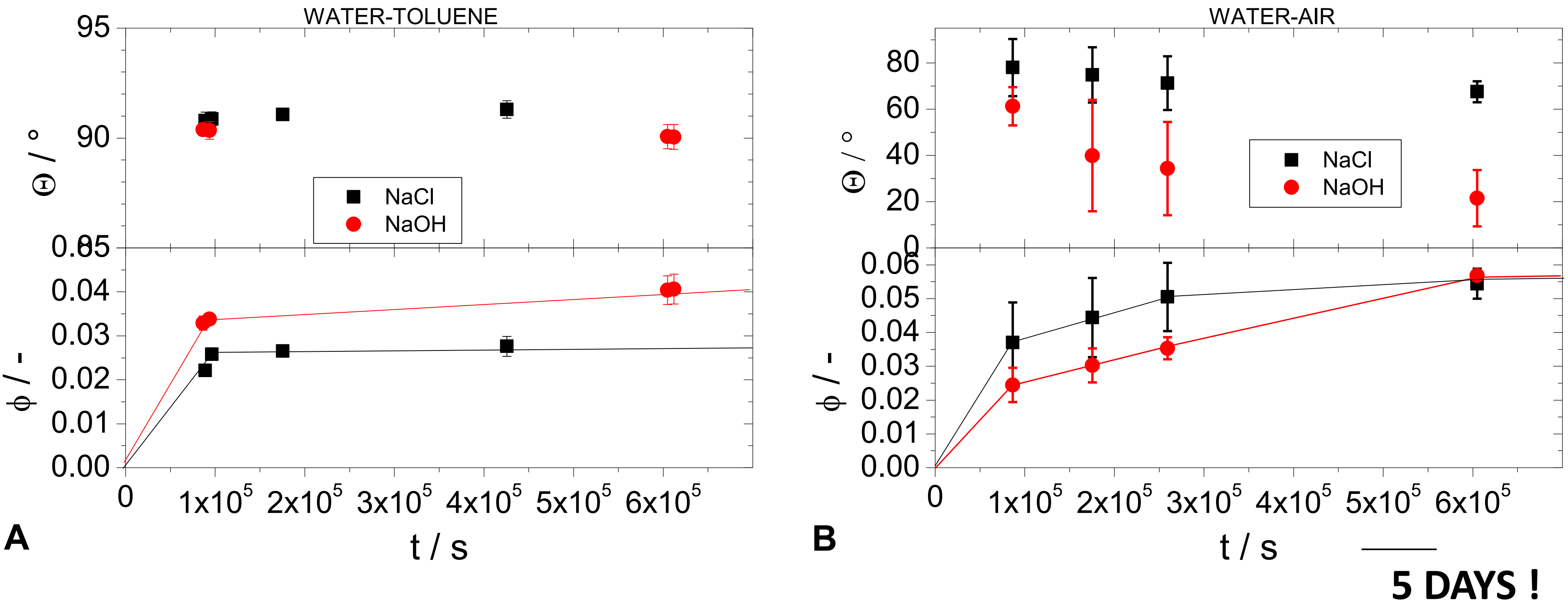
Adsorption occurs in 0.1 M salty water

Water/Air interfaces



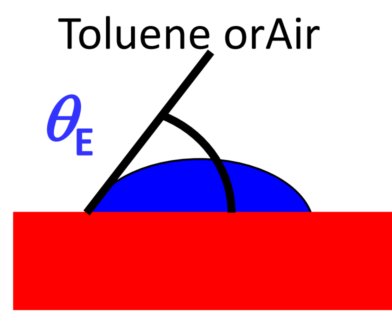
Stocco et al. Soft Matter 2014

Surface coverage ϕ and Contact angle Θ

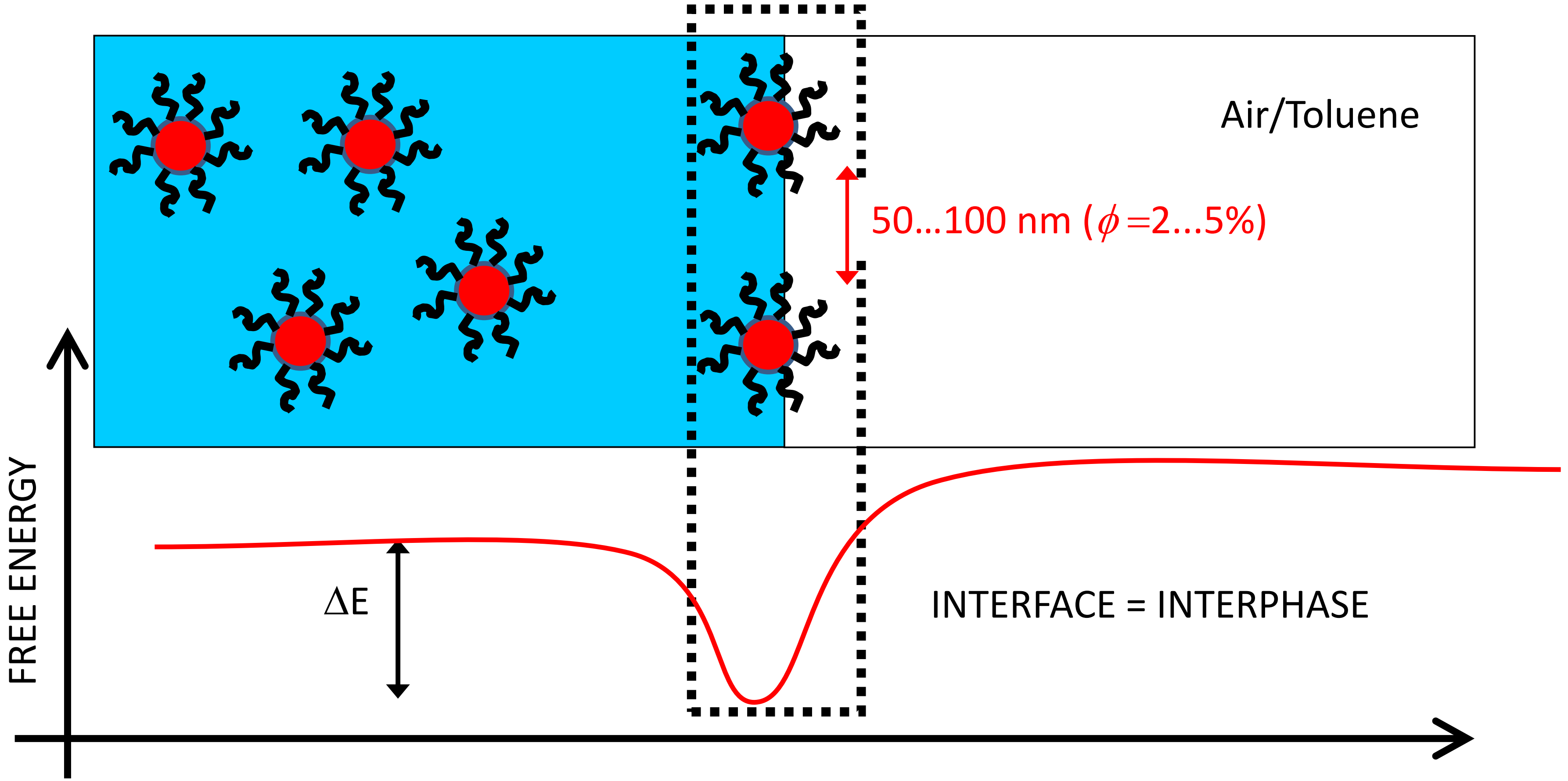


	Water in toluene	0.1 M NaCl in toluene	0.1 M NaOH in toluene
θ_E	93.0 ± 1.1	91.5 ± 1.4	87.4 ± 1.0
Θ		91.3 ± 0.4	90.0 ± 0.6

	Water in air	0.1 M NaCl in air	0.1 M NaOH in air
θ_E	53.3 ± 0.9	52.2 ± 0.7	53.1 ± 1.2
Θ		67.5 ± 4.6	21.5 ± 12.2



Surface coverage ϕ reveals ΔE



Knowing the Bulk conc. (c_B) and finding the Surface conc. (c_S), one might define:

$K = c_S/c_B = \exp(-\Delta E/kT)$

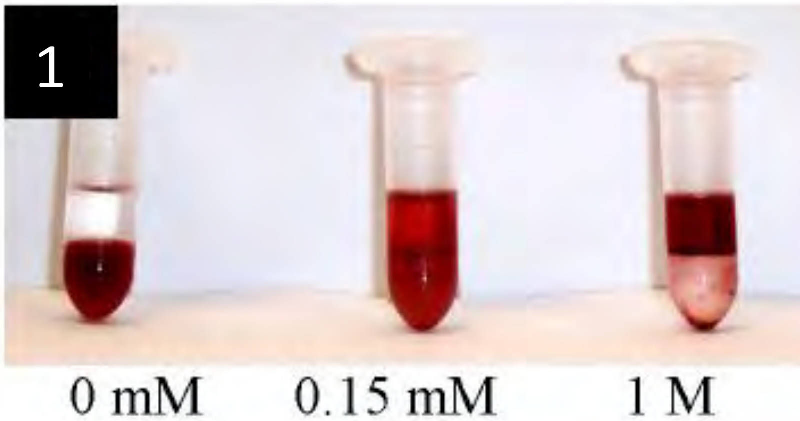
ΔE = ca. 6 kT (→ crossing)

Wetting- single particle

$$-\Delta E_w = \pi\, R^2 \gamma (1 \pm \cos\Theta)^2$$

= ca. $10^2 \ldots 10^3$ kT (→ adsorption)

Crossing Observations

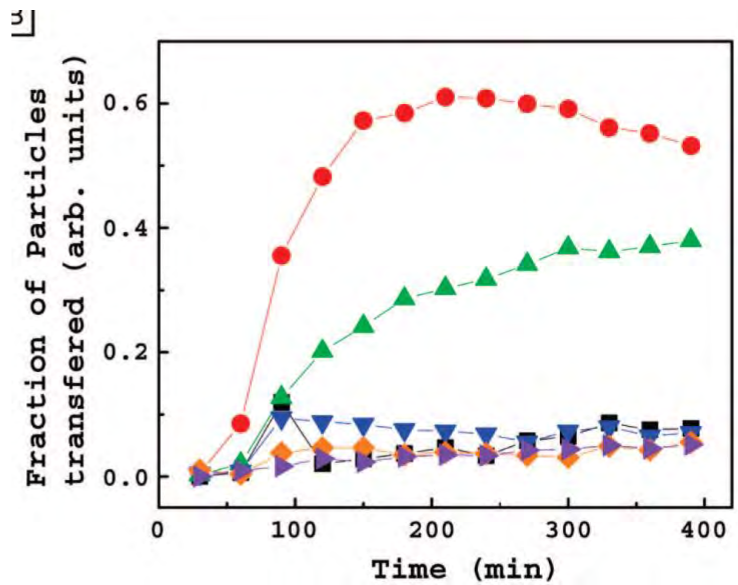


Water to Toluene
at room T by adding NaCl salt

Replacing salty water with pure water,
NO reversible transfer!

Free energy E (+NaOH) < E(in Toluene) < E (in Water)

Crossing------------ adsorption



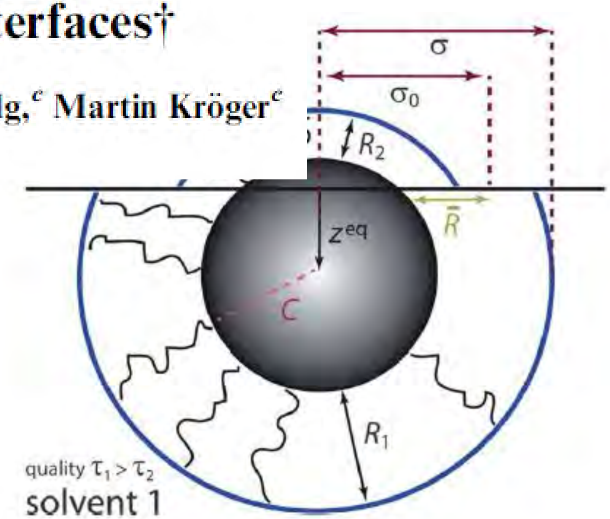
Edwards et al. Angewandte Chemie 2008, J. Phys Chem C 2008

Total Energy $E = E_W + \ldots$

+DLVO (electrostatics + VdW)

+**Adsorption of core-shell nanoparticles at liquid–liquid interfaces†**

Lucio Isa,[*a] Esther Amstad,[a] Konrad Schwenke,[b] Emanuela Del Gado,[b] Patrick Ilg,[c] Martin Kröger[c] and Erik Reimhult[ad]



$$f_i^{\mathrm{int}}/k_BT = \frac{N}{\phi}[(1-\phi)\ln(1-\phi) + \chi_i\phi(1-\phi)],$$

χ_{FH} (Flory-Huggins parameter, solvent quality)

\+ **Hydrophobic coating- and surface active solvent-mediated self-assembly of charged gold and silver nanoparticles at water–air and water–oil interfaces†**

Lijun Xu,[a] Guobin Han,[b] Jiawen Hu,[*a] Yan He,[a] Jiangao Pan,[a] Yongjun and Jiannan Xiang[a]

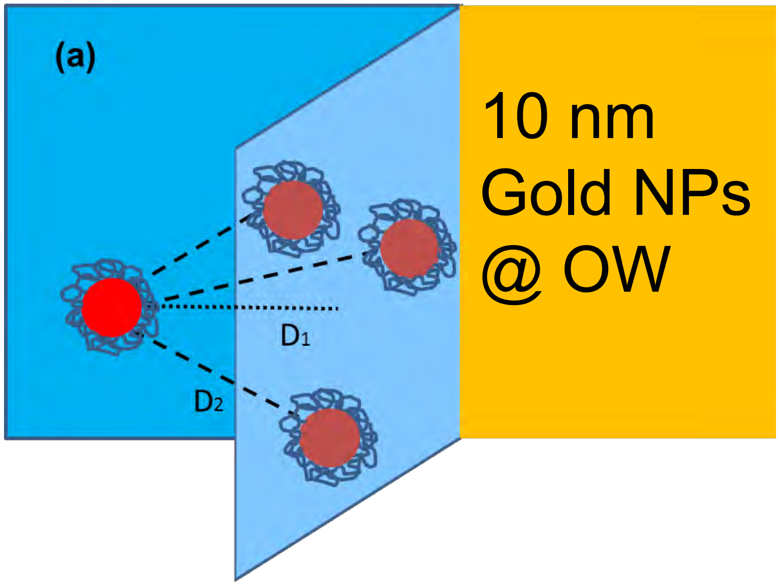
E_{HB}

(hydrophobic attraction close to the interface)

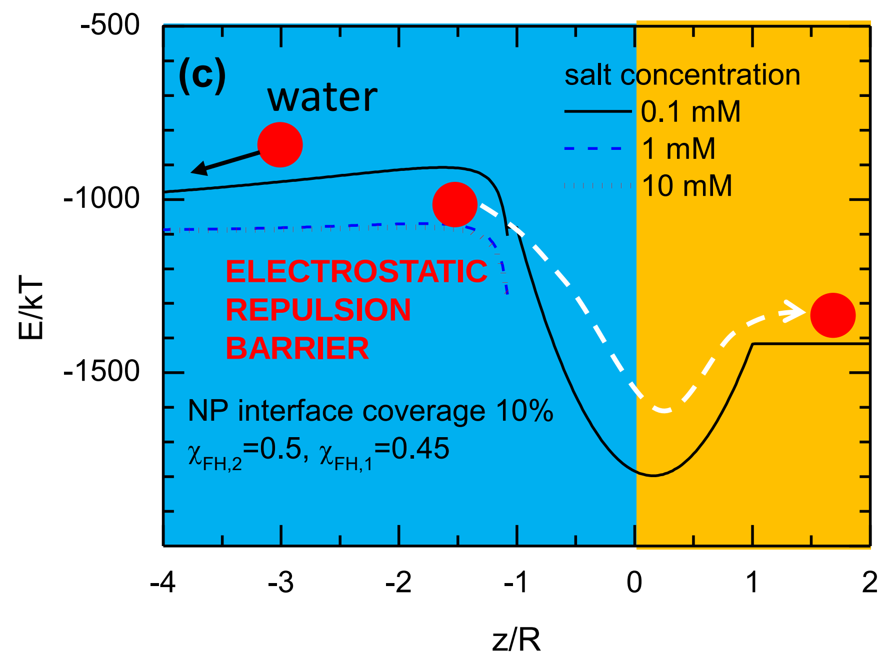
Fig. 1 Digital photograph of a 40 nm gold colloid covered with hexane without (left) and with the addition of 28.6 vol.% of ethanol (right).

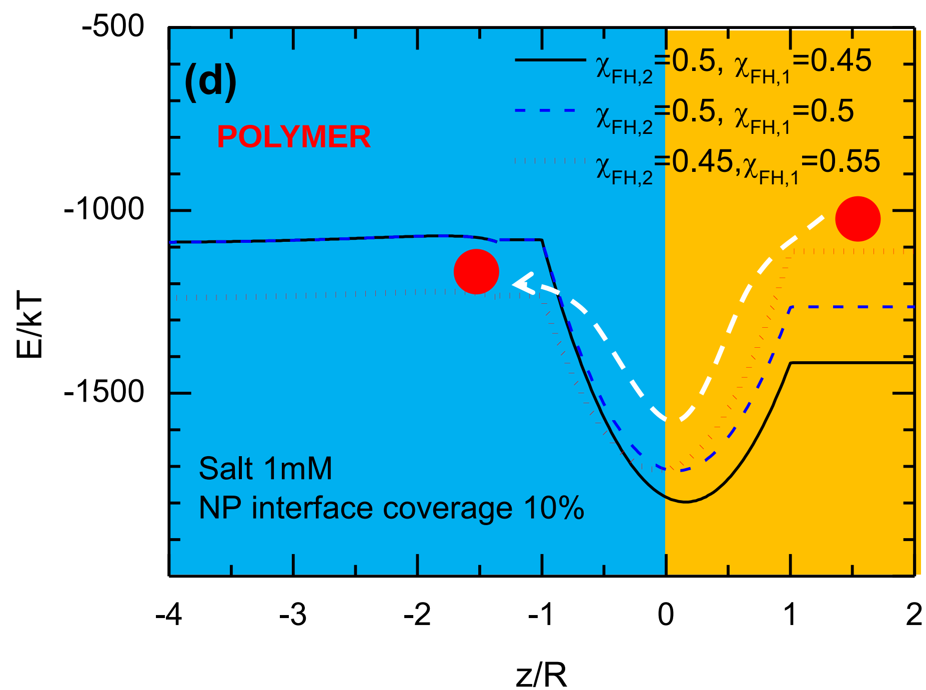
Stocco et al. Angewandte Chemie 2012

$$E(z) = E_W + E_{DLVO} + E_{POLYMER} + E_{HB}$$



Stocco et al. Angewandte Chemie 2012





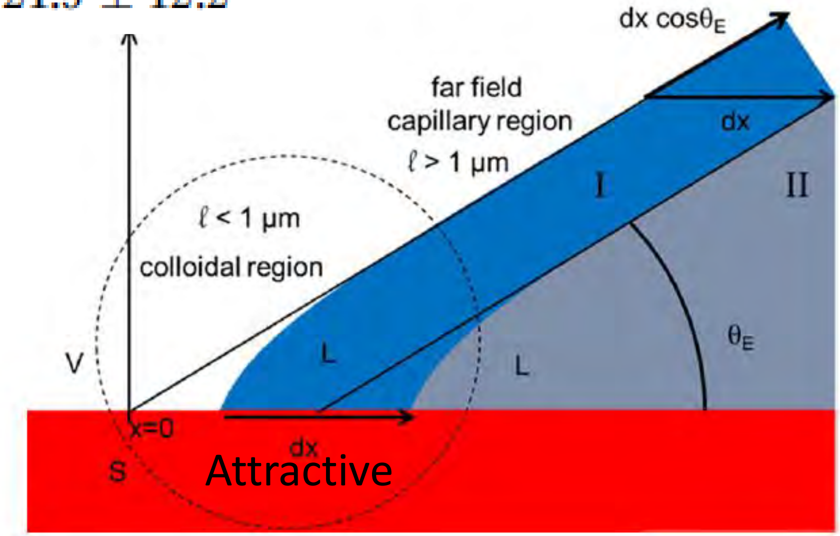
…in agreement with crossing experiments…

Still the minimum is too deep, repulsion between NPs at the interface?

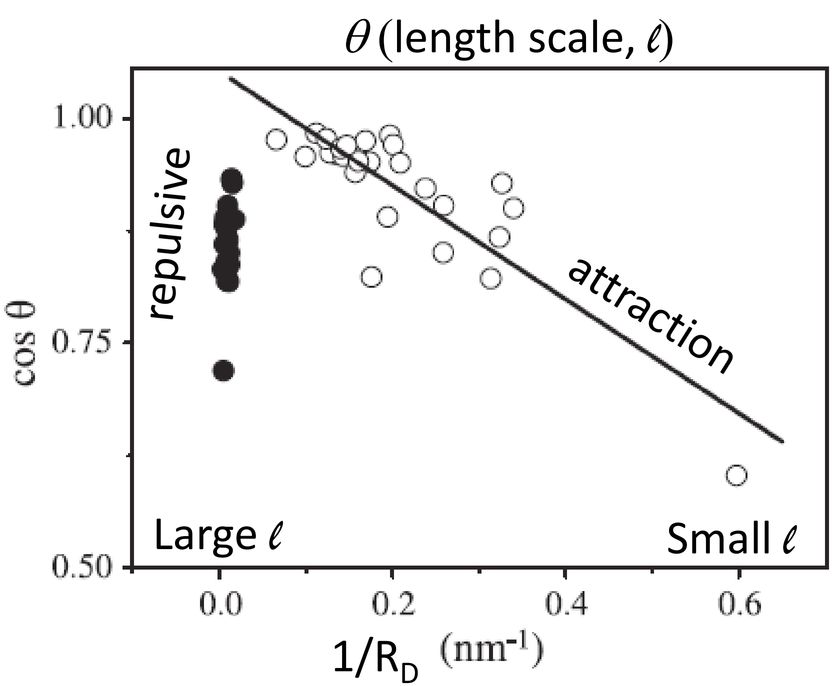
Contact angle - Wetting *vs* Colloidal Forces

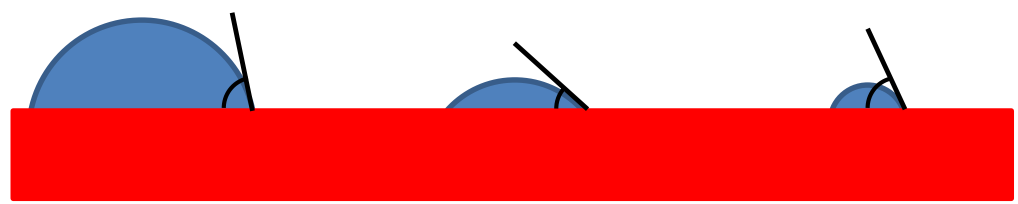
	Water in air	0.1 M NaCl in air	0.1 M NaOH in air
θ_E	53.3 ± 0.9	52.2 ± 0.7	53.1 ± 1.2
Θ		67.5 ± 4.6	21.5 ± 12.2

Capillarity rules the large length scales. Long-range surface interactions
(VdW, Electrostatics..) become important the small length scales



Stocco, Möhwald Langmuir 2015





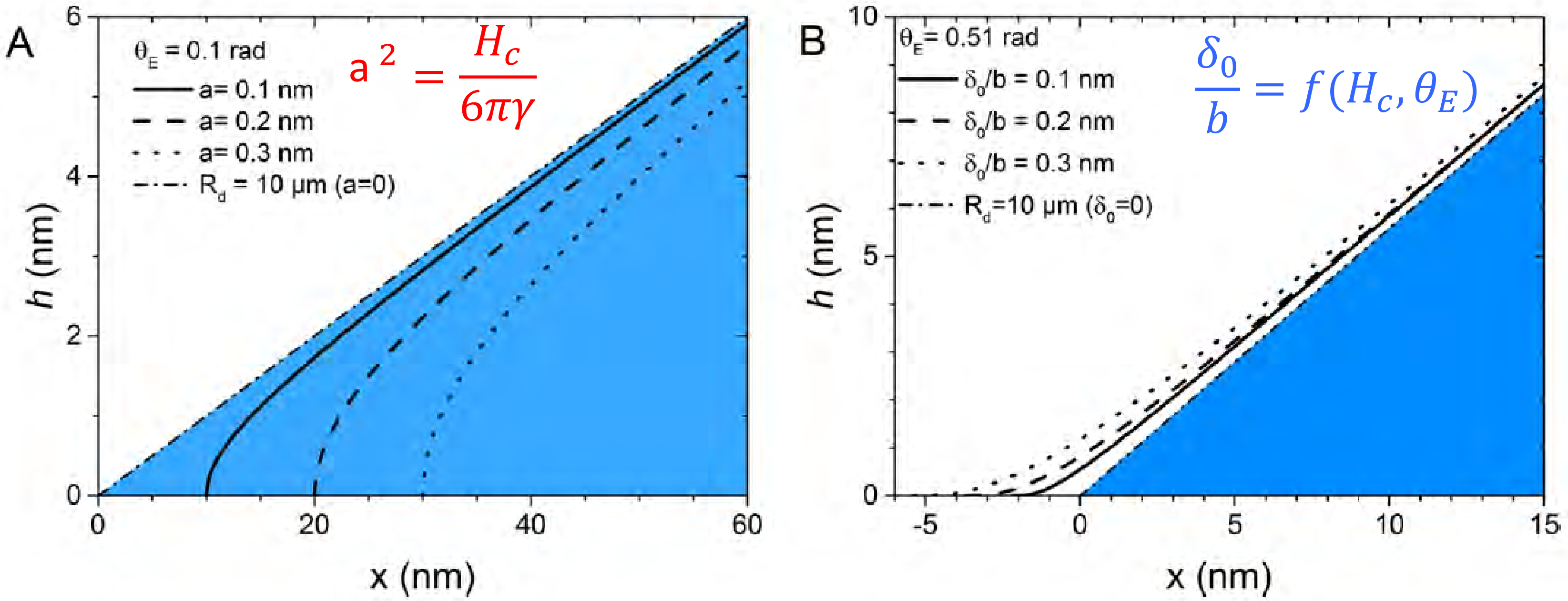
θ (length scale)
Nanodrops, nanobubbles

Lohse et al.Rev Mod Physics 2015

Particle radius sets the scale of wetting

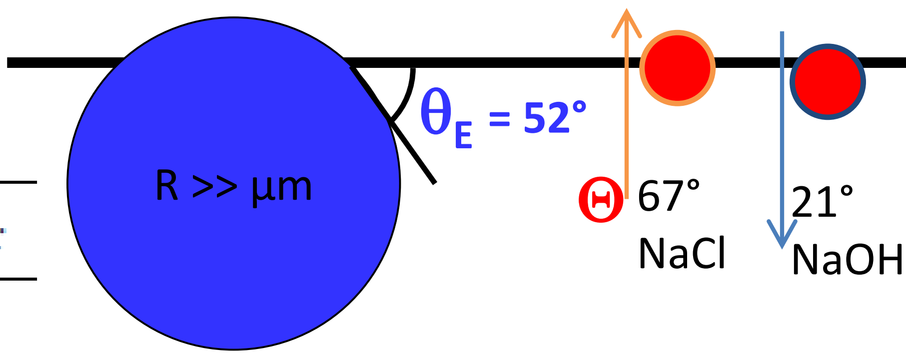
Long range Van der Waals

Stocco, Möhwald Langmuir 2015



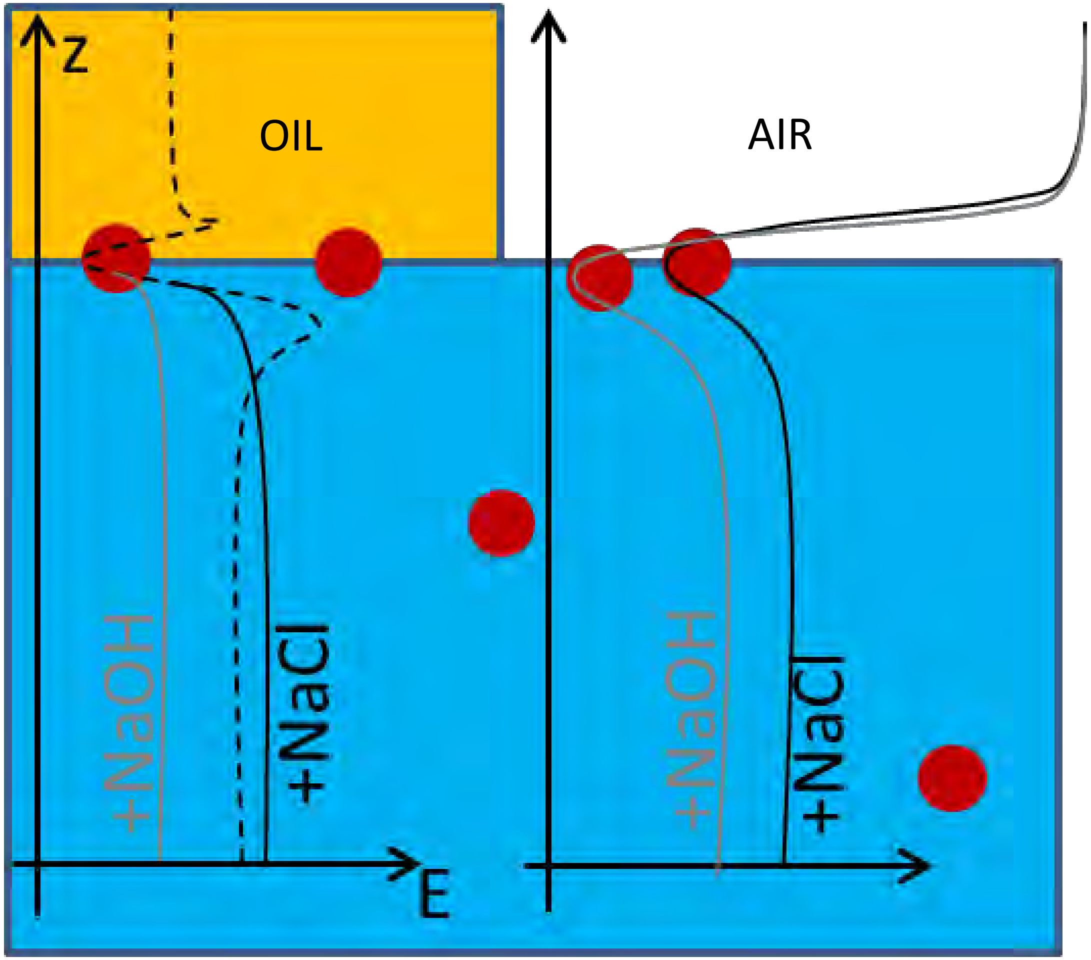
Attraction long range interactions
Increase of local contact angle ($\ell \rightarrow 0$)

Repulsion interactions,
Decraese of local contact angle($\ell \rightarrow 0$)



	0.1 M NaCl in air	0.1 M NaOH in air
θ_E	52.2 ± 0.7	53.1 ± 1.2
Θ	67.5 ± 4.6	21.5 ± 12.2
	Attraction	Repulsion

Summary

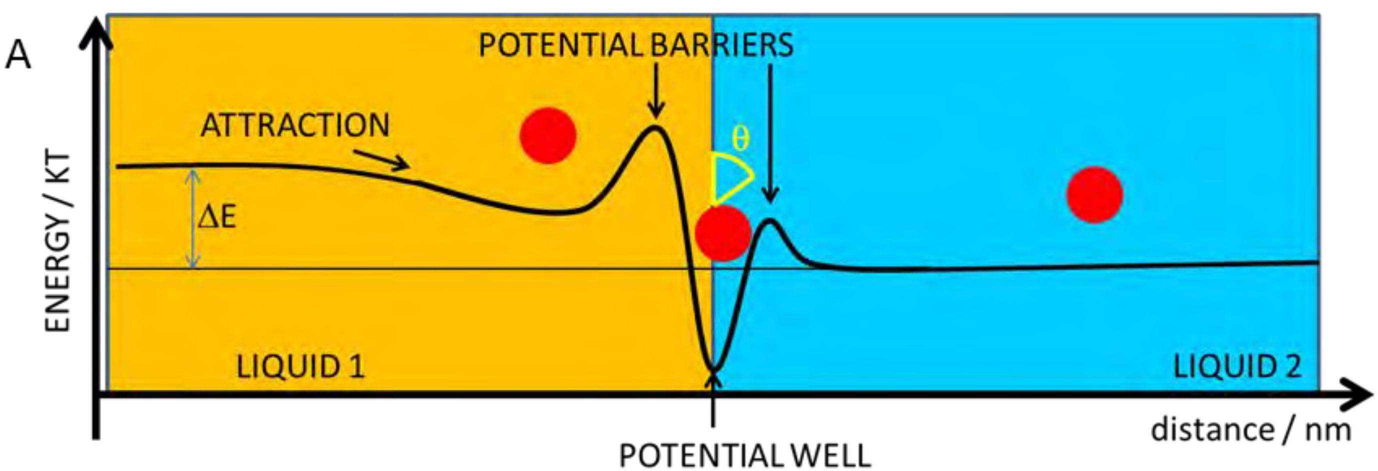


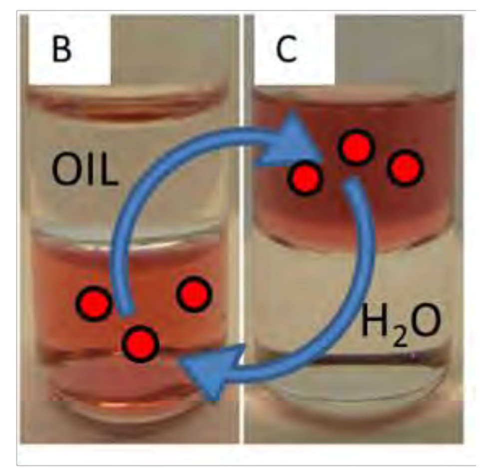
Stocco et al. Soft Matter 2014

Conclusions

» Very slow and low adsorption onto Fluid Interface
» Ellipsometry: Energy landscape & Wetting
» Electrostatic energy barrier
» Phase Transfer can be finely triggered

» Role of Long range surface forces on Wetting & transfer





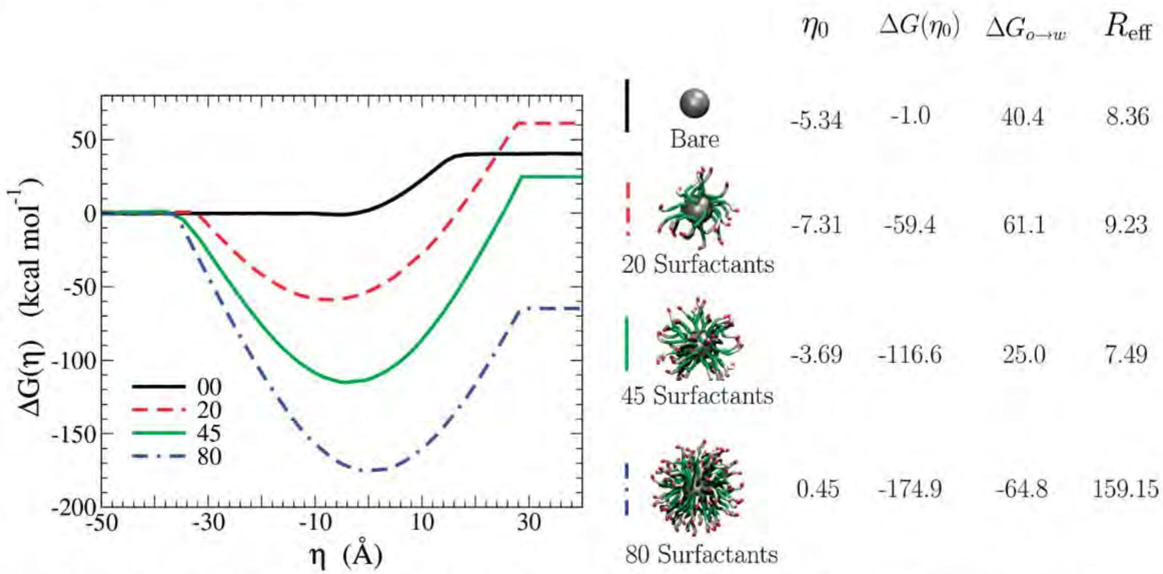


Figure 4. The free energy profiles of the four NP systems. All the NPs show surface activity, which is augmented with surfactant functionalization. The equilibrium positions (η_0, in Å), free energy minima ($\Delta G(\eta_0)$, in kcal mol^{-1}), oil to water transfer free energies ($\Delta G_{\mathrm{o}\to\mathrm{w}}$, in kcal mol^{-1}) and the effective radii (R_{eff}, in Å) from eq 4 are given to the right. Details on how accurate values for η_0 are obtained may be found in the Supporting Information.

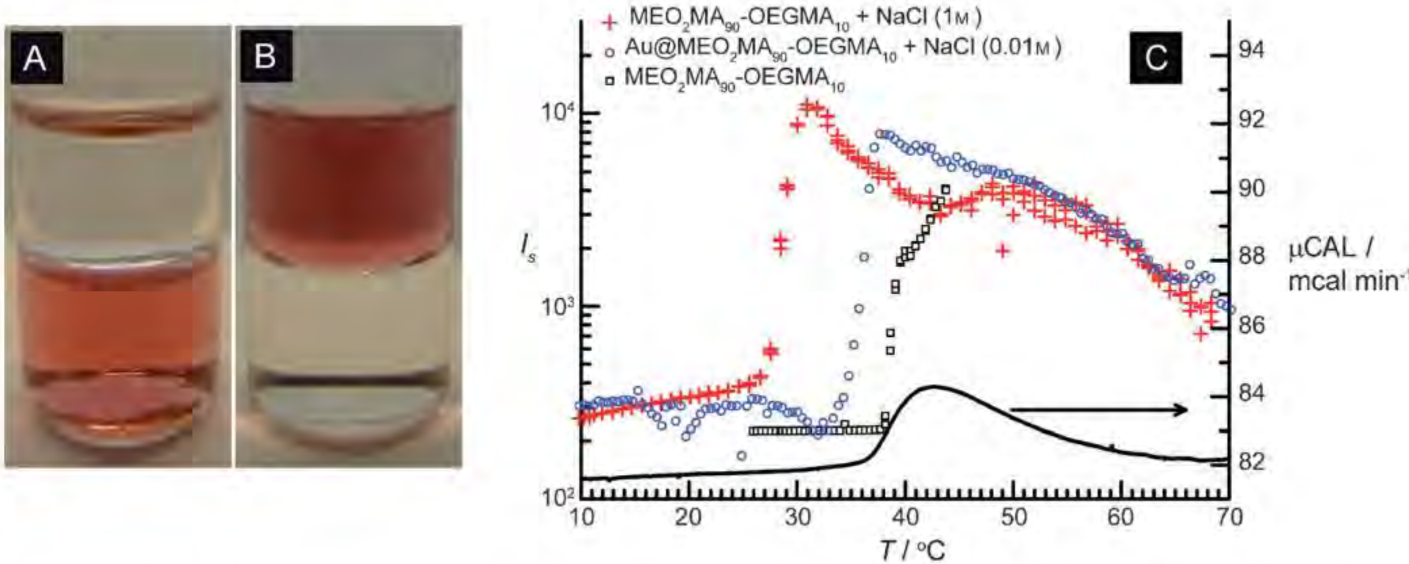


Figure 1. A) Au@MEO$_2$MA$_{90}$-co-OEGMA$_{10}$ NPs well dispersed in water (at room temperature) with a clear toluene phase on top and B) NP transfer to toluene upon adding salt under stirring. The NP concentration in water is 50 mg L^{-1}. C) Temperature-dependent light scattered intensity profiles of MEO$_2$MA$_{90}$-co-OEGMA$_{10}$ copolymer (10 g L^{-1}) in pure water (squares) and 1 M NaCl solution (crosses) and Au@MEO$_2$MA$_{90}$-co-OEGMA$_{10}$ NPs with 10 mM NaCl solution (50 mg L^{-1}, circles). The black curve shows microcalorimetry raw data for the polymer in water. The heating rate ($\delta T/\delta t$) is 6 °C h^{-1}.

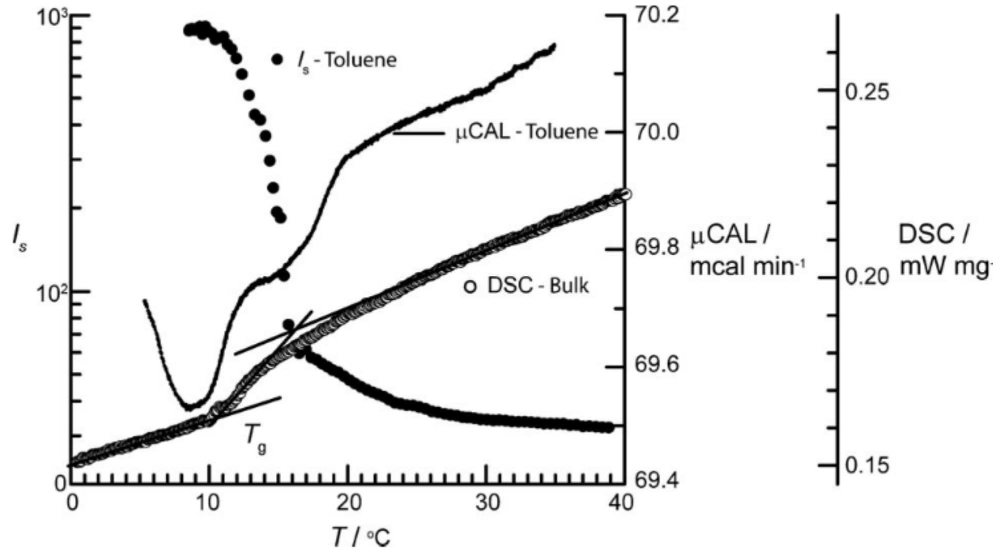


Figure 3. Temperature-dependent light scattered intensity of dispersions of Au@MEO_2MA_{90}-co-$OEGMA_{10}$ NPs in toluene (50 mg L^{-1}, $\delta T/\delta t = 6\,°C\,h^{-1}$) (solid circles). Microcalorimetry raw data of MEO_2MA_{90}-co-$OEGMA_{10}$ copolymer in toluene (10 g L^{-1}, $\delta T/\delta t = 6\,°C\,h^{-1}$) (blue curve). Differential scanning calorimetry (DSC) raw data of dry MEO_2MA_{90}-co-$OEGMA_{10}$ ($\delta T/\delta t = 600\,°C\,h^{-1}$) (red open circles).